

Solid State Unidirectional Photoisomerization of (β -Substituted Ethyl)bis(disubstituted Glyoximato)(L)cobalt(III) to the α -Substituted Ethyl Complexes (L = Pyridine or Primary Amine)

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Photoisomerization of β -cyanoethyl- and β -(methoxycarbonyl)ethyl-bis(disubstituted glyoximato)(L)cobalt(III) (L = pyridine or primary amines) to the α -substituted ethyl complexes occurred in the solid state, but the reverse ($\alpha \rightarrow \beta$) isomerization was not observed, despite the fact that Co-C bond cleavage occurred.

Although solid state reactions of organic compounds are well documented,¹ organometallic solid state reactions have rarely been studied.^{2,3} To our knowledge, reactions accompanying a genuine rearrangement of chemical bonds have not been reported so far in this field.

We now report that isomerization of (β -substituted ethyl)-bis(disubstituted glyoximato)(L)cobalt(III) (L = pyridine or primary amine) to the α -substituted ethyl complexes occurs on

visible light irradiation of the sample in the solid state and the reverse ($\alpha \rightarrow \beta$) isomerization does not proceed.

When a 1% KBr disk of (β -cyanoethyl)bis-(dimethylglyoximato)(pyridine)cobalt(III) was irradiated with sunlight or a sun lamp, the absorption intensity at 2237 cm^{-1} (ν_{CN} of the β -cyanoethyl complex) decreased and that at 2204 cm^{-1} (ν_{CN} of the α -cyanoethyl complex) increased with irradiation time (Figure 1). The rest of the i.r. spectrum

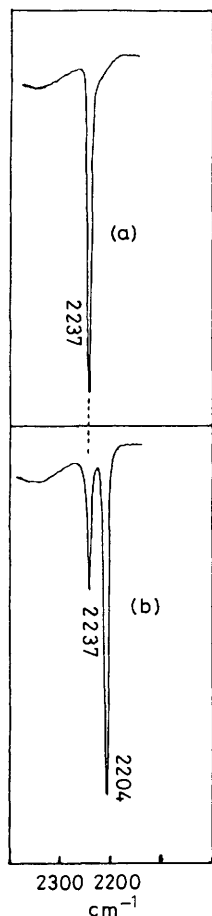


Figure 1. Infrared spectra (CN stretching region) of (1-py-β) (a) and the sample irradiated with a 400 W sun lamp for 4 h (b).

remained almost unchanged. T.l.c. of the crude extracts of the irradiated sample showed the presence of the dealkylated complex (R_f 0), the α -cyanoethyl complex (R_f 0.53), and starting material (R_f 0.59, solvent: acetone-benzene, 1:2), but no oxygen insertion product in spite of the aerobic conditions. The ^1H n.m.r. spectrum of the irradiated sample, after a column chromatographic isolation, showed new signals due to the α -cyanoethyl complex [δ 0.57 [d, $\text{CH}_3\text{CH}(\text{CN})\text{Co}$], 2.24 and 2.26 [$2 \times$ s, $\text{HONC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{NO}$]]⁴ besides those of the starting material (Figure 2). The β -(methoxycarbonyl)ethyl group in bis(dimethylglyoximate)[β -(methoxycarbonyl)ethyl] (pyridine)cobalt(III) (4-py- β) was also proved to transform into the α -(methoxycarbonyl)ethyl group, as follows: new signals due to the α -(methoxycarbonyl)ethyl complex [δ 0.40 [d, $\text{CH}_3\text{CH}(\text{CO}_2\text{CH}_3)\text{Co}$], 2.2 (s, CH_3 of inplane ligand), and 3.49 (s, CO_2CH_3)]⁴ appeared at the expense of signals due to starting material [δ 1.5–2.0 (m, $\text{CH}_2\text{CH}_2\text{CO}_2$), 2.14 (s, CH_3 of inplane ligand), and 3.58 (s, CO_2CH_3)].

In order to clarify the effects of structural variation on this isomerization, photoreactions of several β -cyanoethyl complexes (1-py- β), (1-PEA- β), (1-ADPE- β), (2-py- β), and (3-py- β) were examined by surveying the i.r. absorption intensity ratio of α -cyano and β -cyano groups of the sample irradiated under the standard conditions [a KBr disk (10 mm diameter) prepared from 99 mg of KBr powder and 1 mg of substrate was irradiated at 150 mm from a 400 W sun lamp]. The ratio of α -isomer to β -isomer of a sample was evaluated by

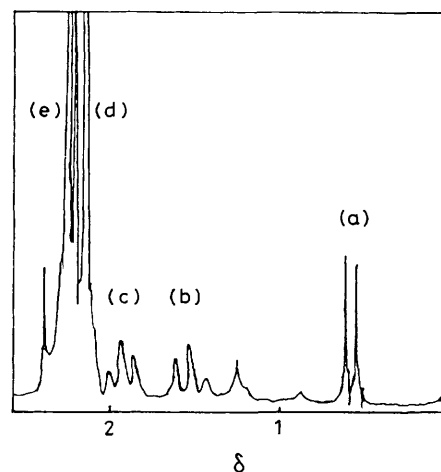
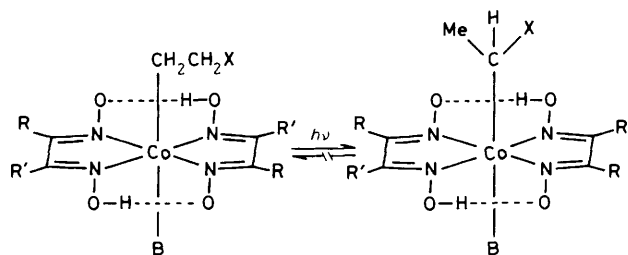


Figure 2. ^1H n.m.r. spectrum of the reaction products isolated after irradiation (10 h) of (1-py- β) with sun light: (a) $\text{CH}_3\text{CH}(\text{CN})\text{Co}$, (b) $\text{CH}_2\text{CH}_2\text{Co}$, (c) $\text{CH}_2\text{CH}_2\text{CN}$, (d) CH_3 of inplane ligand of (1-py- β), (e) CH_3 of inplane ligand of (1-py- α).



(1-py- β)	R = R' = Me, X = CN, B = pyridine	(1-py- α)
(1-PEA- β)	R = R' = Me, X = CN, B = 1-phenylethylamine	(1-PEA- α)
(1-ADPE- β)	R = R' = Me, X = CN, B = 2-amino-1,2-diphenylethanol	(1-ADPE- α)
(2-py- β)	R = Me, R' = Ph, X = CN, B = pyridine	(2-py- α)
(3-py- β)	R = R' = Ph, X = CN, B = pyridine	(3-py- α)
(4-py- β)	R = R' = Me, X = CO_2Me , B = pyridine	(4-py- α)

referring to the calibration curve of absorption intensity ratio of the α -cyano and β -cyano groups for the authentic α/β mixtures. In every β -cyanoethyl complex examined, the β -cyanoethyl group was transformed into a α -cyanoethyl group. The ratio $\alpha:\beta$ increased with irradiation time and the ratio approached a certain value asymptotically. In general, pyridine-co-ordinated complexes gave rather high values [(1-py- β) 1.5, (2-py- β) 1.5, (3-py- β) 9], but complexes co-ordinated with a base bearing strong sigma donor character afforded rather low values [(1-PEA- β) 0.2, (1-ADPE- β) 0.1] under the same conditions. The fact that the curve is asymptotic does not imply a reversible isomerization. In fact, no ν_{CN} due to the β -cyanoethyl complex was detected in the spectrum of the irradiated KBr disk of α -cyanoethyl complexes (1-py- α), (1-PEA- α), (1-ADPE- α), (2-py- α), and (3-py- α). ^1H N.m.r. spectra of the irradiated samples,

(1-py- α) and (4-py- α), after a column chromatographic separation, were entirely in accord with those of the corresponding starting materials. These results clearly indicate that the reverse ($\alpha \rightarrow \beta$) isomerization does not occur. However, this does not imply that the Co-C bonds of α -substituted ethyl complexes are inert to light in the crystalline or solid state, since irradiation of the optically active (*R*)-(1-py- α) ($[\alpha]_{578}^{+68.2^\circ}$, CHCl₃)⁵ and (*R*)-(4-py- α) ($[\alpha]_{578}^{+175^\circ}$, CHCl₃)⁵ afforded racemic (1-py- α) and (4-py- α), respectively.

For comparison with the solid state reaction, photoreactions were examined in benzene solution. But, neither ($\beta \rightarrow \alpha$) nor ($\alpha \rightarrow \beta$) isomerization was observed under Ar atmosphere, and under aerobic conditions, (1-py- α) and (1-py- β) gave the corresponding O₂ insertion products⁶ without isomerization, *i.e.*, α -cyanoethylperoxy and β -cyanoethylperoxy complexes, respectively.

The reasons why the solid state photoisomerization is completely unidirectional, and gives results quite different from those in solution are not clear at present.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

Received, 11th September 1984; Com. 1288

References

- 1 A. Gavezzotti and M. Simonetta, *Chem. Rev.*, 1982, **82**, 1; J. R. Schaffer, *Acc. Chem. Res.*, 1980, **13**, 283; B. S. Green, M. Lahav, and D. Rabinovich, *ibid.*, 1979, **12**, 191; I. C. Paul and D. Y. Curtin, *ibid.*, 1973, **6**, 217.
- 2 J. R. Lyerla, C. A. Fyfe, and C. S. Yannoni, *J. Am. Chem. Soc.*, 1979, **101**, 1351 (chemical exchange); B. E. Hanson, M. J. Sullivan, and R. J. Davis, *ibid.*, 1984, **106**, 251 (chemical exchange); M. Green, J. A. K. Howard, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 869 (phase transition); M. C. Etter and A. R. Siedle, *J. Am. Chem. Soc.*, 1983, **105**, 643 (phase transition); E. J. Miller, T. B. Brill, A. L. Rheingold, and W. C. Fultz, *ibid.*, 1983, **105**, 7580 (co-ordination-dissociation).
- 3 Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada, and Y. Ohgo, *J. Am. Chem. Soc.*, 1981, **103**, 5805; Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada, and Y. Ohgo, *ibid.*, 1982, **104**, 6353; Y. Ohashi, A. Uchida, Y. Sasada, and Y. Ohgo, *Acta Crystallogr. Sect. B.*, **39**, 54; T. Kurihara, Y. Ohashi, Y. Sasada, and Y. Ohgo, *ibid.*, 1983, **39**, 243; T. Kurihara, A. Uchida, Y. Ohashi, Y. Sasada, Y. Ohgo, and S. Baba, *ibid.*, 1983, **39**, 431 (racemization).
- 4 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1967, **89**, 1999.
- 5 Y. Ohgo, S. Takeuchi, Y. Natori, J. Yoshimura, Y. Ohashi, and Y. Sasada, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3095.
- 6 C. Fontaine, K. N. V. Duong, C. Merienne, A. Gaudemer, and C. Giannotti, *J. Organometal. Chem.*, 1972, **38**, 167; C. Gianotti and B. Septe, *ibid.*, 1973, **52**, C36, C45.